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Inspection Manual for the Enforcement of New Source Performance Standards Fuel Gas Fired Combustion Units

Pacific Environmental Services, Inc, Santa Monica, Calif

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INSPECTION MANUAL FOR ENFORCEMENT OF NEW SOURCE PERFORMANCE STANDARDS

FUEL GAS FIRED COMBUSTION UNITS

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16. ABSTRACT

This document outlines the air pollution requirements of Federal New Source Performance Standards for petroleum refinery combustion units which are fired on fuel gas. It is designed to be utilized by agency personnel who are responsible for the enforcement of these regulations. Briefly, the rules are applicable to all combustion units on which construction or modification was commenced after June 11, 1973. If fuel gas is burned in the unit, it is required that the fuel gas be desulfurized to a level of 230 mg/dscm (0.1 gr/dscf) or below, or that effluent combustion gases be treated for sulfur dioxide removal to an equivalent level. This manual also outlines other requirements of the regulation for performance testing, monitoring and record keeping and reporting requirements. Subsequent sections of the document describe types of emission control systems which may be used; procedures for conducting on-site inspections including an inspector's checklist; and approved methods for conducting performance tests.

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1.0 INTRODUCTION

Pursuant to Section 111 of the Clean Air Act (42 USC 1857 et. seq.), the Administrator of the Environmental Protection Agency (EPA) promulgated sulfur in fuel standards for the burning of fuel gas in a new or modified fuel combustion device in a refinery. These proposed standards were issued in the Federal Register of June 11, 1973, and final standards (40 CFR 60.104) became effective on February 28, 1974. The standards apply to all sources whose construction or modification commenced after June 11, 1973. A new emission source is one which is designed and constructed after the formal proposal of new source regulations. New sources include newly constructed facilities, new equipment which is added to existing facilities, and existing equipment which is modified in such a way that results in an increase of pollutant emissions. New source standards limit specific pollutant emissions from categories of sources (such as fossil fuel-fired steam generators, municipal incinerators) which the Administrator determines may contribute significantly to the endangerment of public health and welfare. For these sources, the Act requires the Administrator to promulgate emission limitations which will require installation of the best systems of emission reduction which he determines have been adequately demonstrated. Cost factors are considered in making this determination. Federal new source standards help prevent the occurrence of new air pollution problems, encourage improvements in emission control technology, and provide a mechanism for controlling pollutants which EPA suspects are hazardous, but for which insufficient information is available to regulate such pollutants under other provisions of the Act.

The intent of this report is to provide guidelines for the appropriate enforcement agency in the development of inspection programs for fuel gas combustion systems at a refinery which are covered by New Source Performance Standards (NSPS). Section 2.0 presents the NSP standards as well as a brief outline of related State Implementation Plan (SIP) regulations. Process descriptions for fuel gas treatment plants and fuel combustion devices along with the associated emissions and control techniques are summarized in Section 3.0. Section 4.0 discusses the start-up, shut-down as well as malfunction problems associated with the fuel gas treatment process and fuel gas combustion devices. Detailed inspection procedures required by appropriate personnel during an inspection are presented in Section 5.0. Discussion of performance test requirements is presented in Section 6.0.

2.0 STATE IMPLEMENTATION PLANS (SIP) AND NEW SOURCE PERFORMANCE STANDARDS (NSPS)

This section briefly summarizes state implementation plan regulations and NSPS for the emission of sulfur dioxide from fuel combustion equipment. State implementation plans are federally approved and are designed to prevent local ambient air concentrations from exceeding the National Ambient Air Quality Standards. The NSP standards apply to fuel gas combustion devices whose construction or modification commenced after June 11, 1973.

2.1 EXISTING SOURCES - TYPICAL SIP REQUIREMENTS

A nationwide review of the state implementation plan regulations for the emissions of sulfur oxide from fuel combustion has been recently published by the Strategies and Air Standards Division of EPA,[1] Research Triangle Park. This summary of SIP emission requirements shows the complexity and diversity of SO_2 emission regulations for fuel combustion. Some states control all emission sources equally, while other states prescribe different emission limits for sources according to the fuel used, the geographic location, the size of the source, or the type of source. Following sections highlight typical emission limitations.

2.1.1 Summary of Typical SIP Regulations

A review of Reference 1 reveals that SO_2 emissions are most commonly regulated by limiting the amount of sulfur or sulfur dioxide emitted per unit heat input (LB S/MMBTU, LB SO_2/MMBTU) or by limiting the sulfur content by weight percent that a fuel can contain. SO_2 limitations are also expressed in parts of SO_2 per million parts by volume of stack gas or the weight of SO_2 emitted per hour (LB SO_2/HR). Other methods of limiting SO_2 emissions which appear in the SIPs include requiring a percent control of input sulfur or requiring application of "latest reasonably available control technology" (Florida) or "new proven technologies" (Texas). A few states have SO_x emission limitations addressed directly to petroleum refinery operations or written in terms of H_2S concentrations in refinery process gas streams.

Typical examples of currently approved SO_x regulations for combustion units are:

- The California South Coast Air Quality Management District prohibits the burning of any gaseous fuel containing sulfur compounds in excess of 800 ppm (50 grains per 100 cubic feet) of gaseous fuel, calculated as hydrogen sulfide at standard conditions, or any liquid fuel or solid fuel having a sulfur content in excess of 0.5 percent by weight (Rule 431).

- The Jefferson County, Kentucky, Air Pollution Control District prohibits combustion of any refinery process gas stream that contains H_2S in concentration greater than 10 grains per 100 cubic feet of gas without removal of the H_2S in excess of this concentration (Rule 4.2.1).

Most of the state implementation plans were approved in 1972. Following initial approval of the SIPs, many states began submitting to EPA revisions to their implementation plan, many of which alter the emission limitations. Usually, these revisions are based on additional air quality measurement data or on a more detailed technical analysis of air pollution control strategies. When approved by EPA, these revisions become a part of the implementation plan.

2.2 NEW SOURCE PERFORMANCE STANDARD (NSPS) REQUIREMENTS

The following sections describe in detail the requirements outlined in NSPS for new refinery process gas combustion units. The standards are given in terms of emissions, performance testing, monitoring, record keeping and reporting.

2.2.1 Emission Standards

The NSPS regulations for SO_2 emissions from refinery combustion units appeared in 40 CFR 60.104(a) and state that, "No owner or operator subject to the provisions of this subpart shall burn in any fuel gas combustion device any fuel gas which contains H_2S in excess of 230 mg/dscm (0.1 gr/dscf)."[2] An alternate provision (40 CFR 60.104(b)) to this regulation states, that, "The owner or operator may elect to treat the gases resulting from the combustion of fuel gas in a manner which limits the release of SO_2 to the atmosphere if it is shown to the satisfaction of the Administrator that this prevents SO_2 emissions as effectively as compliance with the requirements of paragraph (a) of this section."[2] In other words, the regulation requires treating of fuel gas or combustion products for any new fuel gas combustion device where the H_2S content of the fuel gas is greater than 230 mg/dscm (0.1 gr/dscf).

2.2.1.1 Exemptions

The proposed standard does not apply to unusual situations, such as emergency gas releases. As stated in the regulation, the combustion of process upset gas in a flare, or the combustion in a flare of process gas or fuel gas which is released to the flare as a result of relief valve leakage is exempted from the requirements of the regulation as stated in Section 2.2.1. However, flares which are maintained to burn a continuous process gas stream are subject to the requirements of the NSPS regulations.

2.2.2 Performance Testing

The owner or operator of a new fuel gas burning device is required to conduct performance tests within a specified period after start-up, and thereafter from time to time as may be specified by the EPA. These performance tests are required in order to demonstrate that the standards are being met by the new device.

2.2.2.1 Initial Performance Test

The initial test of performance of a new facility must be conducted within 60 days after the facility is first operated at its maximum intended rate of operation. However, if the intended rate of operation is not achieved within 120 days of initial start-up, the initial test must nevertheless be conducted within 180 days of start-up. Thirty days must be allowed for prior notice to the EPA, to allow the Agency to designate an observer to witness the test.

Each performance test must be conducted in accordance with the instructions set forth in the regulations (Reference 3), which are discussed in more detail in Section 6 of this manual. The test consists of three repetitions of the specified procedure; performance of the facility is judged acceptable if, for each of the characteristics tested, the average value from the three repetitions is less than the NSP Standard value.

Necessary modifications in the details of the test methods may be made, if approved in advance by the EPA. A written report of the test is to be furnished to the EPA.

2.2.2.2 Subsequent Performance Tests

Subsequent to the initial test, further performance tests may be required from the source at the discretion of the EPA. Alternatively, the Agency may decide to conduct performance tests, for which purpose the owner or operator is required to provide

testing facilities, which include necessary utilities, sampling platforms and safe access to the sampling platform.

Performance testing subsequent to the initial test is most likely to be required when records indicate a relatively high frequency of occurrence of emission levels near, at, or above the NSPS levels.

2.2.3 Monitoring Requirements

The NSP Standards (40 CFR 60.105) require that the owner or operator of any fuel gas burning device in a refinery subject to the provisions of the regulation as discussed in Section 2.2.1 shall install, calibrate, maintain, and operate an instrument for continuously monitoring and recording concentrations of H_2S in fuel gases burned in any fuel gas combustion device, or an instrument for continuously monitoring and recording concentrations of SO_2 in the gases discharged into the atmosphere from the combustion of fuel gases when the owner or operator elects to treat the gases. It should be noted, however, that no H_2S emission monitoring method has as yet been specified in the regulations. Until acceptable monitoring apparatus have been approved, this monitoring requirement can not be enforced.

When a refinery has several fuel gas combustion devices having a common source of fuel gas, monitoring may be done at one location if sampling at this location produces results representative of the H_2S concentration in the fuel to all units. This situation is common in many refineries where a centralized acid gas treatment plant is maintained which treats H_2S rich gases from several refinery process units and routes the treated exit gases to refinery combustion unit fuel supplies.

2.2.4 Record Keeping and Reporting

Any owner or operator subject to the requirements of NSPS is required to maintain records, to furnish certain reports, and to notify EPA of certain plans and occurrences, as discussed below [40 CFR 60.7].

2.2.4.1 Notifications Regarding Commencement of Construction

The owner or operator of any facility subject to the provisions described in Section 2.3 of this report shall submit the Administrator of the EPA a notification of the date of commencement of construction of the affected facility. This notification must be postmarked no later than thirty (30) days after such date.

2.2.4.2 Notifications Regarding Initial Start-Up

The owner or operator is required to furnish to the Administrator of the Environmental Protection Agency written notifications of anticipated initial start-up date and actual start-up date of the new facility. The notification of the aniticpated start-up date must be postmarked no more than sixty (60) days nor less than thirty (30) days prior to that date; notification of actual start-up must be postmarked within fifteen (15) days after its occurrence. In this connection, "start-up" refers to operation of the facility for any purpose.

2.2.4.3 Start-up, Shut-down, and Malfunction Recording

The owner or operator is required to record the occurance and duration of any start-up, shut-down, or malfunction in operation of the fuel gas burning device and to retain the record for at least two years thereafter. The record should also include the nature and cause of any malfunction, together with a notation as to the corrective action and any measures taken to prevent recurrence of the malfunction.

In this connection, "start-up" refers to a renewed operation of the facility for any purpose; "shut-down" means the cessation of operation of the facility for any purpose; and "malfunction" is defined as any sudden unavoidable failure for any component of the plant or of the fuel gas burning device itself to operate in a normal manner. Preventable failures, such as those which may have been caused by poor maintenance or careless operation, or by equipment breakdown due to such causes, are not included in this definition.

2.2.4.4 Records Regarding Performance Testing

The owner or operator is required to make available to the EPA, in order to facilitate conduct of performance tests by the Agency, any records necessary to determine whether performance of the fuel gas combustion is a representative performance at the time of the test. Fuel gas burn rate and hours of operation for any fuel gas combustion device shall be recorded daily. A file of all measurements required for H_2S emissions regulations shall be maintained by the owner or operator. Appropriate measurements shall be reduced if necessary to the units of applicable standard daily, and summarized monthly. The record of any such measurement(s) and summary shall be retained for at least 2 years following the date of such measurements and summaries. These records should also be made available prior to or during inspection of the facility.

2.2.4.5 Quarterly Reports

Quarterly reports are to be filed on the 15th day following the end of each calendar quarter. These reports must include the records of excessive emissions during the calendar quarter in terms of date, time of commencement, and time of completion of each period of excessive emissions, as evidenced by records of monitoring equipment or other observations. The quarterly reports must also include the records of start-up, shut-down, and malfunction during the calendar quarter, with details as to the causes of malfunctions and corrective measures applied.

2.3 APPLICABILITY OF STANDARDS

The NSP Standards are applicable to all new or modified fuel gas combustion devices including process heaters, boilers and flares used to combust fuel gas. A new or modified boiler which has a heat input greater than 250 million BTU per hour may also be subject to the provisions of 40 CFR Section 60, Subpart D. A new or modified source is one on which construction or modification commenced after June 11, 1973, and subject to the following definitions (40 CFR § 60.2).

- "Modification" means any physical change in, or change in the methods of operation of, an affected facility which increases the amount of any air pollutant (to which a standard applies) emitted by such facility or which results in the emission of any air pollutant (to which a standard applies) not previously emitted. The following shall not, by themselves be considered to be modifications.

    (1) Routine maintenance, repair and replacement
    (2) An increase in production rate of an existing facility if that increase can be accomplished without a capital expenditure on the stationary source containing the facility
    (3) An increase in hours of operation
    (4) Use of alternative fuel or raw material if, prior to June 11, 1973, the existing facility was designed to accommodate such alternate use. Conversion to coal required for energy considerations (§119 (d) (5)) shall not be considered as a modification.
    (5) The addition or use of any system or device whose primary function is the reduction of air pollutants, except when an emission control system is removed or replaced by a system which the Administrator determines to be less environmentally beneficial.
    (6) The relocation or change in ownership of an existing facility

- "Commenced" means that an owner or operator has undertaken a continuous program of construction or modification or that an owner or operator has entered into a binding agreement or contractual obligation to undertake and complete, within a reasonable time, a continuous program of construction or modification.

2.3.1 Sulfur Dioxide Emission Standard

The performance standard for emission of sulfur dioxide, applicable to new fuel gas combustion devices, is written in terms of H_2S concentration of fuel gas. This concentration of H_2S in fuel gas is limited to 230 milligrams per dry standard cubic meter (mg/dscm) of fuel gas, or, in English units, 0.1 grains per dry standard cubic foot (gr/dscf). No owner or operator is permitted to burn any fuel gas containing more than the above specified concentration of H_2S in any fuel gas combustion unit. Actual H_2S concentration of fuel gas must be monitored during routine operation of facility. A determination as to whether the facility is in or out of compliance with this regulation is based on the results of performance tests conducted in the manner prescribed in 40 CFR § 60.106 (c).

Since a refinery generally operates several fuel gas combustion units, performance tests must be conducted on the fuel gas going to each applicable combustion device. However, if a refinery has a centralized fuel gas supply system with an acid gas treatment plant for all of the fuel gas streams, then a one point performance test of H_2S concentration at the outlet of fuel gas supply system can be performed to determine compliance for all of the affected combustion units.

The sampling period for the performance test is specified in 40 CFR § 60.106 (c)[2] and is not less than 10 minutes. Since three repetitions are required the total minimum sampling time is 30 minutes.

As discussed in Section 2.2.1 the second provision of the SO_2 regulation [40 CFR § 60.104 (b)][2] may allow burning of fuel gas with an H_2S concentration greater than 0.1 gr/dscf provided that the owner or operator elects to treat the combustion gases so as to reduce the SO_2 emissions to atmosphere as effectively as compliance with the requirements of 40 CFR § 60.104 (a).[2] In order to determine whether the facility is or is not in compliance with the regulation, a performance test should be conducted at the emission point as described in 40 CFR § 60.106 (d).[2] Detailed discussion of this test method will be covered in Section 6.0.

3.0 PROCESS DESCRIPTION, ATMOSPHERIC EMISSIONS AND EMISSION CONTROL METHODS

A refinery, in general, is a large industrial complex consisting of many processes which require fuel combustion units for process heat. Many of the refinery processes produce gas streams which can be used as fuel in combustion units. These gases generally contain a variety of sulfur compounds which in turn can be oxidized to SO_2 and be emitted to the atmosphere from combustion units. The amounts and types of the sulfur compounds in the fuel gases from a unit depend upon the sulfur content of the feedstock to the unit and the process operating parameters such as temperature, pressure or catalyst type.

In order to reduce the sulfur content of these acid gas streams and make them more suitable for fuel usage, refineries utilize amine absorption processes. Normally, one HDS unit will be maintained to treat a number of process gas streams generated at different refinery units and will provide cleaned fuel gas for a number of combustion units. The scope of this section will be to consider the operating conditions, atmospheric emission points and possible emission control systems starting at the inlet to the acid gas treating facility. While the NSPS standards are only aimed at control of new refinery combustion units, it is the operation of the acid gas treater which actually determines what the sulfur content of the fuel gas will be and hence the compliance of the fuel burning source.

3.1 FUEL GAS COMBUSTION SYSTEM

As discussed in the preceeding section several processes such as cracking, coking, hydrocracking and other fractionation units are responsible for the production of refinery fuel gases. These gases may be treated and then used as fuel in combustion units or may be used directly in combustion units.

3.1.1 Acid Gas Treatment Plant

The Acid Gas Treating process uses either diethanolamine (DEA) or monoethanolamine (MEA) in aqueous solution to remove acid gases (H_2S and CO_2) from the process gas stream. Removal is accomplished by a chemical reaction between the acid gases and the chemically basic amine solution. The reaction can be reversed by heating the solution, and this behavior is used to regenerate the treating solution.

A process flow diagram for a typical Acid Gas Treating Plant is shown in Figure 3-1. The process gas containing H_2S (sour gas), is fed to the bottom of the amine absorber where it is brought into counter-current contact with regenerated (lean) amine solution. The treated gas leaves the top of the absorber and is sent to the refinery fuel gas system. The amine-acid gas (rich amine) leaves the bottom of the absorber, is heated by exchange with stripper bottoms, and is sent to the top of the stripper. Acid gas is stripped from the amine by steam generated at the bottom of the stripper by the stripper reboiler. The acid gas and steam leave the top of the stripper, pass through a condenser and enter the separator where the condensed steam is separated from the acid gas. Acid gas from the separator is sent to a sulfur plant where the H_2S is converted to elemental sulfur. The condensed steam is returned to the stripper as a reflux. Regenerated (lean) amine from the bottom of the stripper is cooled by exchange with rich amine and is pumped through an amine cooler back to the top of the absorber. Part of the lean amine is sent through an amine filter to maintain solution cleanliness and a sump is provided for adding or draining solution to or from the system. Further information on acid gas treating can be obtained from References 4 and 5.

The degree of treatment achieved depends mainly on the partial pressure of H_2S in the treated gas in equilibrium with the incoming lean amine. This in turn is a function of operating pressure, the residual H_2S content of the lean amine, the amine concentration, and the temperature. Higher operating pressure results in higher removal efficiency but operating pressure is normally fixed by the pressure required in the fuel gas system, usually about 3.52 kg/cm^2 (50 psig), and the cost of compressing process gas. The H_2S residual concentration in the lean amine is set by stripper operating conditions. Low pressure favors good stripping and the pressure is generally held at a few psig to supply the sulfur plant without the use of compressors. Increasing heat to the stripper reboiler provides more stripping steam and better stripping, but the amount of steam is limited by cost and equipment size. Amine concentration must be maintained within limits and should be checked regularly. Too high an amine concentration leads to excessive stripper bottoms temperature, with corrosion and amine degredation. Low amine concentration can be partially compensated for by increased amine circulation, within equipment limitations, but this increases operating costs. Low amine temperature favors high treating efficiency, and proper cooling of the lean amine depends on adequate sizing and maintenance of the rich amine--lean amine heat exchanger and the amine cooler. The amine cooler may be a fin-fan unit, in which case performance is affected by air temperature, or a cooling water exchanger, in which case cooling water temperature is important.

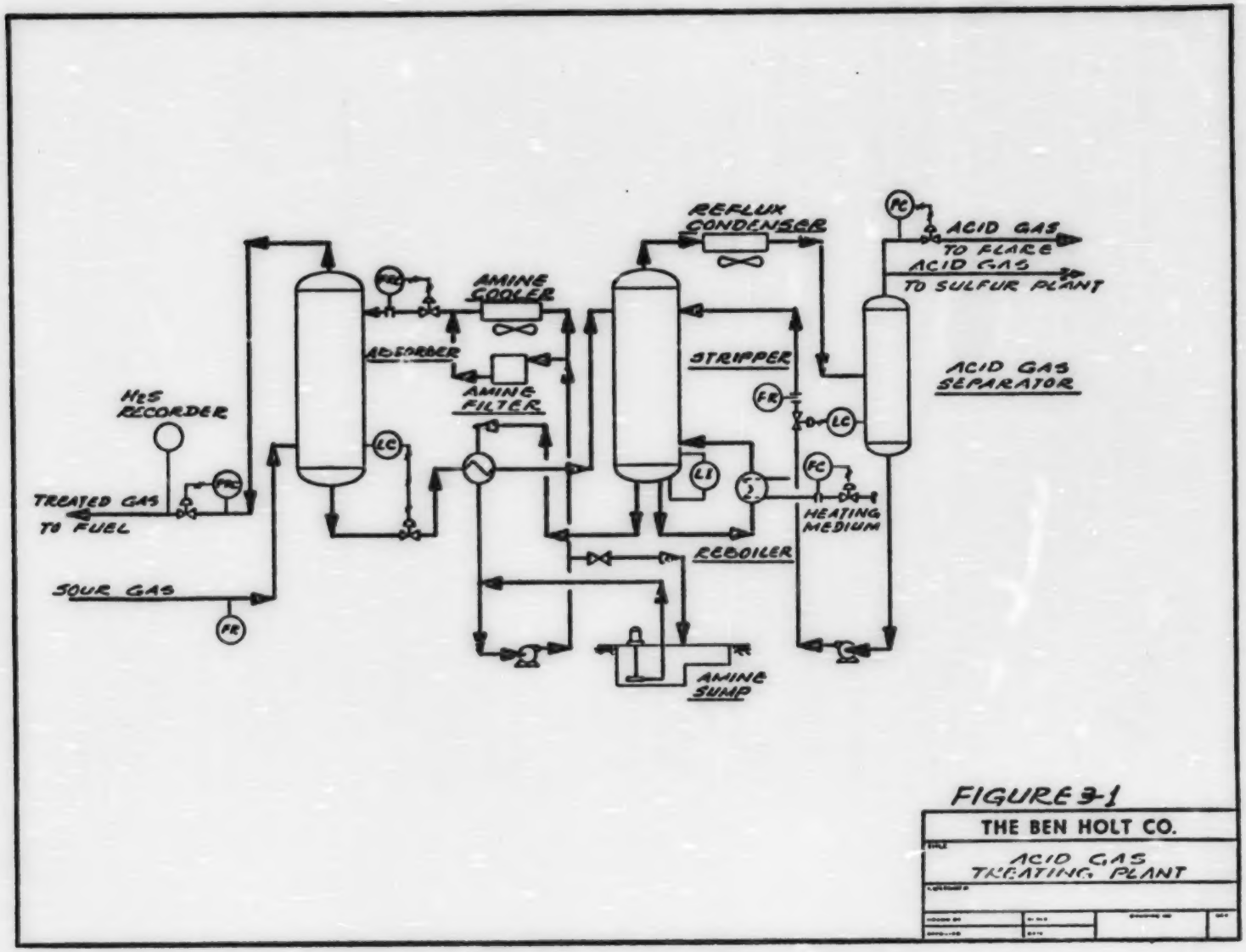

FIGURE 3-1

THE BEN HOLT CO.

ACID GAS TREATING PLANT

3.1.2 Fuel Combustion Units

In the context of this report, an affected fuel combustion unit has been defined at the onset of Section 2.3. A general discussion will be presented to furnish the reader with more information on the types of combustion units used in a refinery and the types of fuels and associated emissions which are typical. Refinery combustion operations involve the use of process heaters to transfer heat to hydrocarbon fluids in heat exchange devices as well as the use of boilers to produce process steam and flares to burn waste gases. Process heaters and boilers are fired by either natural gas, refinery process gas, oil, or a combination of these fuels. Gaseous fuels used are usually mixtures of non-condensible hydrocarbons that for one reason or another are not marketed or further processed.

Figures 3-2 and 3-3 show the types of heaters used typically in a refinery. In most refinery heaters an oil or other petroleum product flows inside the heat exchange tubes. Boilers and reboilers are generally used for the process steam requirements or may be used for power generation. These boilers are either gas, oil and/or coal fired. Use of a particular type of fuel will depend on the availability of the fuel as well as air pollution regulation constraints.

Treated refinery gas leaves the top of the absorber of the acid gas treatment plant and is collected in a fuel gas system as discussed earlier in Section 3.1.1. Treated gas from this fuel gas system is distributed to various combustion units according to their requirements. As an alternative, a refinery may elect to use the refinery gas as it is, i.e. without acid gas treatment, and treat the exhaust gases for reducing the pollutants emitted.

3.2 ATMOSPHERIC EMISSIONS

Except for leaks and malfunctions, the treating plant is not in itself a source of atmospheric emissions. If, however, the plant is not operating efficiently, the treated gas can contain excessive amounts of H_2S and burning the gas can lead to excessive sulfur dioxide emissions to the atmosphere. Also, the acid gas product of the plant has high H_2S concentrations and must be properly disposed of, usually in a sulfur plant.

Combustion units are the ultimate emission source of this system. Most of the sulfur contained in the fuel to the unit is oxidized to SO_2 and leaves the system as combustion gases. Combustion units can also be sources of other emissions which are not

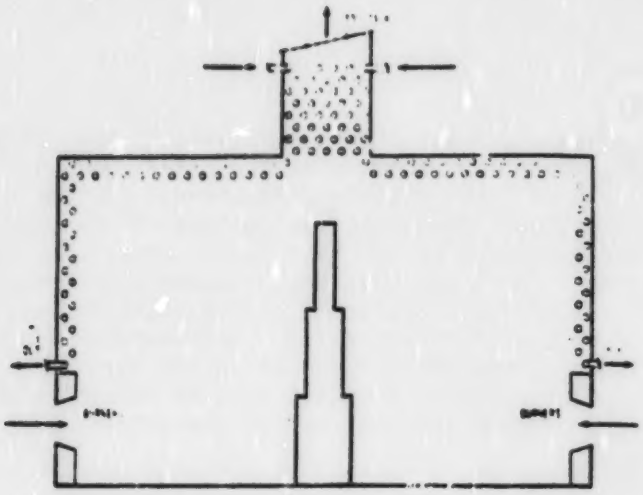

Figure 3-2 A large box-type refinery heater.

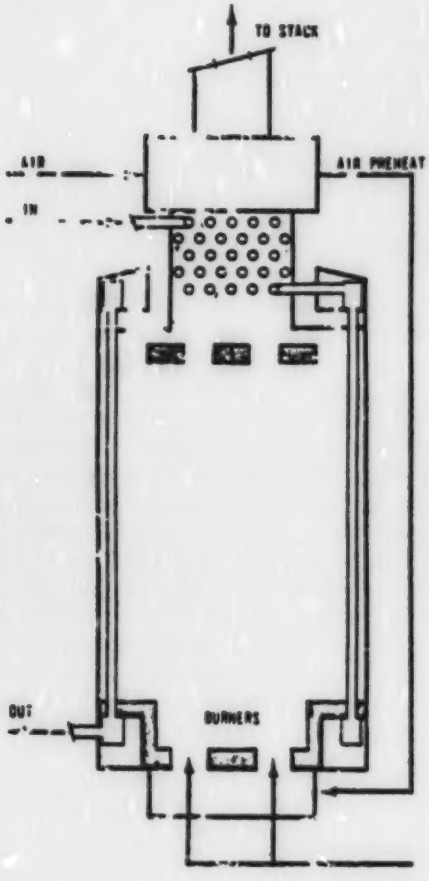

Figure 3-3 A vertical, cylindrical refinery heater

regulated by NSPS. They can emit both visible and non-visible air contaminants. Visible contaminants are principally liquid and solid particulates. Non-visible contaminants include oxides of nitrogen and carbon. Inorganic ash content of oils and coal after nearly complete combustion of these fuels constitutes the particulate emissions. At times when soot blowers are in operation, particulate matter concentrations in exit gases increase markedly. Emissions of oxides of nitrogen from combustion equipment result from fixation of atmospheric nitrogen in the fire boxes. Combustion equipment has been traditionally associated with visible smoke plumes caused by unburned carbon and organics.

3.3 POLLUTION CONTROL METHODS

The acid gas treatment plant itself can, in a sense, be considered as a control process for the removal of H_2S from the refinery gases before they are burned. The stripped acid gases can be sent to a sulfur plant where H_2S is converted to elemental sulfur. Several process technologies are available for fuel oil, gas, and coal desulfurization in order to remove the sulfur from these fuels. When untreated fuels are used directly in combustion units, a wet scrubber system or some sort of concentration/neutralization system in conjunction with a sulfur plant can be utilized as after gas treatment in order to reduce SO_2 emissions. Cyclones and electrostatic precipitators can be used to remove particulate matter from the exhaust gases of the combustion units when coal is the major fuel used. A proper control of excessive air requirement may reduce NO_x emissions to a degree.

3.4 PROCESS INSTRUMENTATION

Although there may be variations from one unit to another, the process instrumentation shown in Figure 1 is typical for an acid gas treatment plant. A flow recorder measures total sour gas flow to the absorber and a pressure recorder-controller on the treated gas maintains absorber pressure. Treated gas quality is monitored by an H_2S recorder. Amine circulation rate is set and maintained by a flow recorder-controller on lean amine to the absorber and rich amine leaves the absorber under level control. Since amine circulates on a closed loop between the absorber and stripper, the level indicator in the bottom of the stripper is an indication of the amine inventory in the system. Reflux rate to the stripper is set by flow control of the heating medium to the stripper reboiler, with all condensed reflux returned to the stripper under level control on the separator. A recorder in the return line records reflux flow rate. Although not shown, temperature indicators are provided at key points throughout the plant

including the lean amine fuel to the absorber.

Process instrumentation for a combustion device will depend upon the type of unit, the use of the unit, and the type of fuel used. Parameters generally controlled are fuel input rate, fuel to air ratio, excess air requirement, fire-box temperature, and flow rate of the fluid being heated.

4.0 START-UP/MALFUNCTIONS/SHUT-DOWN

4.1 START-UP

Acid gas treating plants are sufficiently reliable in their operation that they can be scheduled for maintenance turnaround when the units they serve are scheduled for a turnaround. This generally results in a plant start-up once in a period of one to two years. The treating plant is normally brought on-stream ahead of the units it serves so that start-up does not produce any additional emissions over a normal operation.

Start-up procedure for a fuel combustion device depends upon the type of combustion equipment used. Start-up procedure will vary from unit to unit, but, in general, emissions are higher during start-up than during normal operations. However, this excessive emission is exempted from regulation as long as reporting requirements are met. The owner or operator subject to the provisions of NSP Standards is required to furnish the Administrator written notification of the anticipated date of initial start-up of an affected facility not more than 60 days or less than 30 days prior to such date. The owner or operator is also required to furnish a notification of the actual date of initial start-up of an affected facility within 15 days prior to such date (Reference 6).

4.2 MALFUNCTION

Fire and equipment ruptures are considered to be emergencies and first consideration must be given to safety. They are, by their nature, unpredictable but occur rarely and their contribution to long term polution problems is not great. For the acid gas treatment plant power failures can result in plant shut-down, loss of amine circulation, loss of heating medium, loss of cooling, or loss of control system operation. Since plants are designed to fail safe, the usual result is the flaring of sour process gas and some acid gas product. If the power failure lasts only a few minutes, as is often the case, it may be possible to return the plant to full operation in a matter of minutes. Power outages of longer duration generally result in plant shut-down. The frequency and duration of power failures varies greatly from region to region, and may vary with season.

Malfunctions within the process are usually related to a failure in the supply of a sufficient quantity of cool, well-stripped, lean amine to the absorber. The lean amine flow rate is set by the operator to match the acid gas rate in the sour gas feed. If either the flow rate of the sour gas or the concentration of acid gas is

increased, the lean amine rate should be increased.

Types of malfunction in combustion units generally include:

- Fuel to air ratio variation
- Excessive air supply
- Fire-box refractory damage
- Erosion or corrosion of tubes in combustion units

The owner or operator is required to maintain for a period of 2 years a record of the occurence of any malfunction that may occur in operation of the facility (Reference 6).

4.3 SHUT-DOWNS

Scheduled shut-downs should not result in the production of additional emissions over normal operation. By continuing stripper operation for a period of time after stopping the process gas feed, the Acid Gas Treating plant can be emptied of acid gas. A small amount of acid gas may remain in the lines to the sulfur plant and this should be vented to a flare.

Neither should scheduled shut-downs of combustion units result in the production of additional emissions over normal operation. However, any emissions which occur during emergency shut-downs are generally permitted by regulation. The owner or operator is required to maintain for a period of 2 years, record of the occurence of any shut-downs that may occur (Reference 6).

5.0 INSPECTION PROCEDURES

An air pollution inspection consists of entering a refinery to determine if the equipment or processes meet the standard and comply with the rules and regulations of the air pollution control agency. The inspection process also includes a spot-check of selected records maintained by the operator. The enforcement official must observe, in a qualitative manner, the items associated with atmospheric emissions. The condition and type of equipment, and general housekeeping all influence the emission rate. Equipment design is a major factor that must be reviewed at the time the construction permit or operating permit applications are evaluated.

The importance of plant inspection as a field operations activity that provides for the systematic detection and observation of emission sources cannot be overemphasized. The whole process of inspection follows certain rules and guidelines which are discussed briefly in the following sections. Additional information regarding inspection procedures, field surveillance and enforcement guidelines is presented in References 7 through 10.

5.1 CONDUCT OF INSPECTION

There are four important components in the conduct of inspection of a given equipment or a process.

- Formal Procedure (e.g. use of credentials, ask to see appropriate official)
- Overall inspection process (e.g. review of process and records)
- Safety precautions and procedures
- Frequency of inspection

5.1.1 Formal Procedure

Prior to actual on-site inspection, the inspector should investigate any available data on plant operations. In preparation for the inspection the official should obtain the following data:

- Information for each major source (from an air pollution point of view) including process descriptions, flow

diagrams, estimates of emissions, applicability of standards, and previous related enforcement actions

- Plot plans showing disposition of all major units at the facility

- Business and ownership data including names of responsible management personnel

At the time of inspection, the inspector must have with him the credentials showing his identity as an official of an air pollution control agency. He should arrange an interview with the management of the refinery. The interview with refinery managers and equipment operators can verify data gathered and clarify any misunderstanding with regard to the information reviewed prior to the inspection.

5.1.2 Overall Inspection Process

Some inspections, especially initial ones, are comprehensive, designed to gather information on all equipment and processes of the refinery. Others are conducted for specific purposes such as:

- Obtaining information relating to violations

- Gathering evidence relating to violations

- Checking permit or compliance plan status of equipment

- Investigating complaints

- Following up on a previous inspection

- Obtaining emissions information by source testing

An initial refinery inspection lays the groundwork for evaluating potential emissions of pollutants from a given source and for assessing the relative magnitude of pollution control problems requiring correction, reinspection, or further attention. The initial inspection has two phases: a refinery survey and a physical inspection of the equipment and processes. After this inspection is complete, routine surveillance continues. Periodic reinspections are scheduled and occasional special-purpose inspections (unscheduled) may be required.

During the initial survey, the inspector examines the possible effects of emissions on property, persons and vegetation adjacent to the source; he may also collect samples or specimens

that exhibit possible pollution-related damage. Sensory observations (odor detection) are also made.

The NSP Standards for the facility were given in Section 2.0. The details have been given in Section 2.2, where the records related to the process which must be maintained were also discussed. The inspector must also review these records kept by the operator.

An aid to the inspector is the information incorporated in applications to operate the equipment. The permit status of the equipment should be routinely checked to detect any changes in equipment or process that might invalidate an existing permit or conflict with variance conditions. Similarly, alteration of equipment is frequently detected by discrepancies in the equipment description or by changes noted on engineering applications in the permit file.

5.1.3 Safety Equipment and Procedures

All refineries have standard safety procedures for employees and visitors. These procedures also concern the inspector. The inspector is accompanied to the unit or units to be inspected by the air pollution representative within the plant or by such other informed refinery personnel as he might indicate. Personal protection is necessary in many of the industrial locations that an enforcement officer may be required to visit. The inspector should wear a hard safety hat while in a plant. He should wear rubber gloves and goggles when necessary. In the event of fire in the area of inspection, the inspector must leave the plant immediately, and remain outside the area until the "All Out" signal is sounded. The inspector should be accompanied by another person and two persons should remain together until the job is completed. He must not smoke or carry cigarette lighters which ignite when dropped within an oil refinery. He should use only approved flashlights in oil refineries.

5.1.4 Frequency of Inspections

Because of the complexity of the petroleum industry, unit processes must be inspected systematically and regularly. The frequency of reinspection is based upon the findings during the initial inspection and the recommendations of the inspector and his supervisor. These recommendations obviously depend on whether or not the "good" maintenance practices from the pollution standpoint are followed by the operator. Further, the frequency would depend on the overall inspection load of the control agency for the whole district. The reinspections are scheduled so that they can be completed within a month. The number of reinspections assigned

per district is based on the estimate that all required inspections can be completed within one year.

The enforcement officer may have occasion to inspect the process out-of-schedule because of complaints or violations. In these cases, he does not make a formal inventory reinspection, but uses the copy of the previous inventory record (equipment list) from his files as a check on status of the permit, compliance, or other situation.

5.2 INSPECTION CHECKLIST

Data obtained during an inspection can be summarized on forms similar to the ones shown on the ensuing pages. These forms also serve as a record of inspection.

5.2.1 Facility Identification

Facility Name _____

Facility Address _____

Mailing Address _____

Telephone Number _____

Nature of Business _____

Date of Last Inspection _____

Responsible Person to Contact _____

Persons Contacted at Plant Site _____

Inspectors _____

Source Code Number _____

Date of Inspection _____

5.2.2 Opacity Observations

Emission Source _____

Pre-entry observation:

Average percent equivalent opacity from Method 9 observation

_____

Reading ranged from _____ to _____% opacity.

Name of observer (inspector) _____

Post-entry observation: _____

5.2.3 Odors

Area _____ None Faint Strong (Circle one)

Area _____ None Faint Strong (Circle one)

Area _____ None Faint Strong (Circle one)

5.2.4 Acid Gas Treating Plant

a) Design input capacity (e.g. flow rate of sour gas into the absorber) _____ cu m/min (cfm)

b) Actual flow rate of sour gas into the absorber _____ cu m/min (cfm)

c) Output of unit (flow rate of treated gas) _____ cu m/min (cfm)

d) Actual flow rate of acid rich gas to flare _____ cu m/min (cfm)

e) Actual flow rate of acid rich gas to Sulfur recovery plant (or other unit)_____ cu m/min (cfm)

f) Concentration of H_2S in

- Sour gas entering the acid gas treatment plant _____ mg/dscm (gr/dscf)
- Treated gas going to fuel gas system _____ mg/dscm (gr/dscf)
- Acid rich gas leaving the acid treatment plant _____ mg/dscm (gr/dscf)

g) Disposal technique used for acid rich gases — Sulfur Plant / Flare / Other / None (Circle One)

h) Any leakages? (specify location) _____

i) Amine absorber's pressure _____

j) Type of absorber used _____

k) Concentration of absorber used (e.g. 10 percent solution in water) _____

l) Temperature of cool "lean" amine entering the absorber _____ °C

m) Temperature of hot "rich" amine leaving the absorber _____ °C

n) General Remarks

Condition of various temperature, pressure, and flow ratio controls and last maintenance date _____

General remarks on amine stripper _____

Remarks on amine sump _____

Any isolated streams of sour gas untreated for H_2S removal and recovery? (specify location) _____

Condition of filters (the cool "lean" amine is filtered before entering the absorber) _____

5.2.5 Fuel Gas Combustion Unit

a) Type of unit (circle one) Boiler Process Heater
Flare Other (specify)

b) Design capacity (size of the unit) _____ MM K-cal/hr (MM BTU/hr)

c) Design fuel gas burn rate _____ scm/hr (scf/hr)

d) Actual fuel gas burn rate _____ scm/hr (scf/hr)

e) H_2S concentration of fuel gas _____ mg/dscm (gr/dscf)

f) Heat content of fuel gas _____ Kcal/cu m (BTU/cf)

g) Is fuel gas treated in acid gas treatment plant? Yes ____ No ____ (Check one)

If answer to g) is No, only information for j) through r) must be collected.

h) Location of H_2S monitoring equipment _____

i) Technique of H_2S monitoring (e.g. effective sampling) _____

j) Types and amount of auxiliary or additional fuels used (if any)

Natural Gas	_____	scm/hr (scf/hr)
Fuel Oils (specify number)	_____	liters/hr (gal/hr)
Coal	_____	LT/hr (tons/hr)
Other	_____	specify units

k) Characteristics of auxiliary or additional fuels used (if any)

Fuel Used	Heat Content	Sulfur Content	Ash Content (Specify Units)
Natural Gas	___Kcal/cu m (BTU/cf)	___mg H_2S/dscm (gr H_2S/dscf)	_____
Fuel Oil	___Kcal/liter (BTU/gal)	___% S by wt.	_____
Coal	___Kcal/kg (BTU/lb)	___% S by wt.	_____
Other	___(Specify Units)	___(Specify Units)	_____

l) Are exit gases from combustion unit treated for SO_2 removal?
Yes _____ No _____ (Check One)

m) Type of exit gas treatment (e.g. wet scrubber) _____

n) Location of SO_2 monitoring equipment _____

o) Quantity of SO_2 in the exit gases _____ kg/hr (lb/hr)

p) Equivalent H_2S concentration in the fuel gases _____ mg/dscm (gr/dscf)

q) Exit gas flow rate _____ scm/min (scfm)

_____ acm/min (acfm)

r) Exit gas temperature _____ °C (°F)

s) General remarks (if any) _____

5.2.6 Air Pollution Control Equipment

Acid Gas Treatment Plant Wet Scrubber Other

A) Acid gas treatment plant (checklist already presented)

B) Scrubber

a) Evidence of corrosion and wear _____

b) Pressure drop across the tower _____

c) Type of scrubbing slurry used (e.g. lime, limestone slurry) _____

d) L/G (liquid/gas) ratio _____

e) Effluent disposal system _____

f) Estimated collection efficiency _____ %

g) Location of SO_2 monitoring equipment _____

h) Quantity of SO_2 in the exit gases _____ Kg/hr (lb/hr)

i) Equivalent H_2S concentration in fuel gases _____ mg/dscm (gr/dscf)

5.2.7 Records of Operation

a) Are records of operation kept? Yes_____ No _____ (Check one)

b) Quality of records (circle one) Good Fair Poor

c) Regulations regarding record keeping being followed? (see Section 2.2.4 for regulations)

d) Initial Start-up _____

e) Startup, malfunction, and shutdowns _____

f) Performance testing _____

g) Quarterly reports _____

5.2.8 Operational Aspects

a) Plant operating within specified limits? Yes No If No, describe

b) Any changes or modifications to equipment? (modifications without Agency's approval?) Yes No If Yes, describe

c) Evidence of lack of maintenance Yes No If Yes, describe

d) Location of continuous monitoring equipment for measuring H_2S concentration in the treated fuel gas _____

e) Other general remarks (specify) _____

5.3 INSPECTION FOLLOW-UP PROCEDURES

After the completion of the inspection, the inspector must determine the compliance status of the source based on the data collected. If the collected data are not sufficient for the compliance evaluation, he must contact appropriate refinery personnel to acquire required data. As a precaution, the validity of data must be checked. If an inspection indicates that a source is not operating in compliance with applicable regulations, the inspector should follow established agency procedures regarding notice of violation, request for source test, and related matters.

The various items which could result in a determination of non-compliance would include:

- Concentration of H_2S in excess of 230 mg/dscm (0.1 gr/dscf) in the fuel gas after acid gas treatment which is burned in the fuel gas combustion device without any after treatment for SO_2 removal.
- Concentration of SO_2 in excess of equivalent H_2S concentration of 230 mg/dscm (0.1 gr/dscf) in the fuel gases resulting from the combustion of untreated fuel gas and after appropriate control method.
- Monitoring equipment for H_2S in fuel gas or for SO_2 in exit gases not in operation.

The inspector should check to ensure that permits have been granted for all applicable processes and equipment and their modifications. For any later public complaints, he should determine cause of complaint, record pertinent data, issue violation notices if appropriate, and ascertain adequacy of plans for prevention of future incidents. He periodically should review emergency procedure plans and make sure that all shut-down procedures are being implemented during periods of process curtailment while coordinating with other agencies participating in pollution reduction efforts. As a part of inspection follow-up procedures, he should also check to see that engineering, procurement, installation, and testing of equipment is proceeding according to the approved plan.

In the case of incident and complaint investigations, court actions, and variance board activity, the inspector will need the data collected during his previous inspection visits of the facility.

For example, the point of emission of excessive odors may be traced from an incident described in an operator's log or from an odor survey record.

6.0 PERFORMANCE TEST

The NSP Standards require a performance test of any new fuel gas combustion device. In order to guarantee the validity of the test, an inspection team will be present at the facility for observation. The team should consist of three enforcement personnel with the following areas of responsibility during test period.

- Monitor process operating conditions from the control room.
- Make visible observations of process operations from the plant area.
- Monitor emission testing procedures from the test site.

Each team member will fill out checklist type data during the test and will submit a report including analysis of the data and indication of any upset conditions which may have affected the test.

6.1 PROCESS OPERATING CONDITIONS

For the purpose of obtaining source test data which is truly representative of the operating characteristics of the Acid Gas Treatment Plant or the fuel combustion device being tested, it is extremely important that the test be conducted at or above the maximum production rate at which the unit will normally be operated. In certain cases, the EPA may feel that conditions other than the maximum operating rate of the plant should be used to achieve valid test results. In such cases, the EPA will designate conditions at which source performance testing is to take place. In all cases, inspectors must personally verify that the plant is operating at the specified conditions, and that a stabilized, steady state of operation has been reached. Such verification should be made with the plant operator and refinery manager, and inspectors should observe process controls (i.e. gauges, rate-meters, and recorders) to determine that operating conditions are as designated. During the source test, inspectors should periodically check operating conditions of the plant, carefully noting any changes in the operating parameters such as temperature, pressure, or sour gas flow rate.

Since the NSP standards apply to the fuel gas which is to be burned in a combustion device, inspectors must make certain that the sampling is done at the point where the treated gas is provided to the combustion unit or, if all gases are treated, at the point where the gas is released to the refinery fuel supply line. As most refinery fuel gas lines are operated at rather high pressures, it is important to ascertain that proper precautions are used in sampling these lines, including the use of pressure reduction valves where necessary.

In the event that the owner or operator is using untreated fuel gas in the combustion device and is treating the exit gases from the combustion device in an appropriate manner to control the SO_2 emissions within the specified limits of the regulation, inspectors should make certain that the sampling is done for the SO_2 emissions at the point where exit gases are discharged from the air pollution control system or at the point of discharge from the combustion device if no control system is present.

Inspectors must verify that provisions exist for logging and recording the operating rate as well as the hours of operation of the units concerned on a daily basis.

6.2 PROCESS OBSERVATIONS

6.2.1 Acid Gas Treatment Plant

Untreated refinery fuel gas contains appreciable quantities of hydrogen sulfide (H_2S) and must therefore be treated to remove this component prior to the burning of the refinery gas in process units, in order to prevent formation of excessive emissions of sulfur dioxide. Acid Gas Treatment Plants remove CO_2 and H_2S from the refinery fuel gas stream by absorption in an absorbing solution. The solution is then separated from the de-sulfurized refinery fuel gas and the H_2S and CO_2 are reclaimed by heating the absorbing solution under reduced pressure. The H_2S and CO_2 components may then be sent to a sulfur recovery plant for reclamation, while the regnerated absorbing solution is recycled.

Since the Acid Gas Treatment Plant is a closed system, no pollution control devices are installed as a general rule, however, inspectors should make sure that samples are taken from the centroid (or a point near the center) of the fuel gas line at a point just after the treated gas is released from the plant.

At the time the performance test is conducted, the inspector should make careful notation as to the existing layout of the treatment plant, type of absorbing solution, and operating parameter ranges of the plant (such as pressures, temperatures and flow rates). Inspectors should also determine that a provision exists for monitoring (by instrumental means) the concentration of hydrogen sulfide in the treated fuel gas just after it is released into the refinery fuel gas line. If possible, a photographic record should be made of the principle process units as any modifications to the plant will likely change the results of future performance tests. Inspectors should determine what means of disposal are utilized for the H_2S which has been separated in the treatment plant (most often it will be transported to a sulfur recovery plant for removal of elemental sulfur). The equipment checklist is the same as that which appears in Section 5.2.

6.2.2 Fuel Gas Combustion Device

The inspector should first check the overall configuration of the combustion devices (i.e. to check if they have acid gas treatment plant or if they have a pollution control system for the exit gases). In any event, he should note the type of any other additional or auxiliary fuels that the refinery may be burning along with the fuel gas. General information regarding the combustion unit such as type of equipment and other parameters as presented in Section 5.2 of this report should be carefully observed.

Inspectors should also determine that a provision exists for monitoring (by instrumental means) the H_2S concentration in the treated fuel gas just after it is released into the refinery fuel gas line. Inspectors should also check any SO_2 monitoring equipment downstream of the combustion unit or pollution control system, whichever may be the case, when untreated gases are burned in the combustion device. As a general observation practice for combustion units, inspectors should check and observe the stack associated with the combustion device for possible visible contaminants. Often the presence of a detached, visible plume indicates a sulfuric acid or SO_2 mist emission. Operating parameters and control of these parameters for the pollution control system should be carefully checked.

6.3 EMISSION TEST OBSERVATIONS

Emission source testing discussed here concerns determining compliance of new sources with EPA New Source Performance Standards (NSPS). During source testing operations, field inspectors should periodically spot check testing procedures, equipment, and data to make certain that the test is valid.

All performance tests should be conducted while the unit being tested is operating at or above maximum production rate at which unit will normally be operated. If EPA Administrator feels that other conditions should be used to achieve valid test results, such will be used as basis for testing.

6.3.1 Traversing (EPA Method No. 1, Reference 6)

Of first importance is the selection of a sampling point and determination of a minimum number of traverse points to ensure the collection of a representative sample. Inspectors should make certain that the sampling site selected is a minimum of eight (8) diameters downstream and at least two (2) diameters upstream from any disturbance to the flow of gases within the duct or stack which

is being sampled. Such disturbances are commonly caused by expansions or contractions, bends, visible flames, observable cross-members, or other entering ducts.

6.3.2 Stack or Duct Gas Velocity Determination (EPA Method No. 2, Reference 6)

In the determination of gas velocity within the duct or stack, it should be made certain that all data from each traverse point is carefully and accurately recorded as this is the basic information used to determine the stack flow rate. Each point determined by Method 1 shall be identified by a number and the following information shall be recorded: Velocity head in inches of water; stack (duct) pressure in inches of Mercury; and temperature (unless the total temperature variation with time is less than 10°C. Care should be taken to determine that a type "S" pitot tube is used to obtain the velocity head readings and that this tube is of sufficient length to reach all traverse points. The pitot tube should be graduated with temporary markings (i.e., tape or chalk marks) such that each traverse point may be reached by successively moving the tube deeper into or withdrawing it further from the duct or stack being sampled. All tubing and connectors between the pitot tube and the inclined manometer or draft gauge should be tight and leak-free. An inclined manometer or draft gauge should be used to obtain velocity head readings from the pitot tube. Make certain that this gauge is filled with sufficient colored liquid to give readings throughout its range of calibration, and that the manometer liquid level is adjusted to read "zero" with the end of the pitot tube shielded from incidental breezes prior to beginning the velocity head measurement. Periodically check to make sure that no constriction occurs in the hose connections during the course of the velocity head measurement.

The most common means of stack temperature measurements is by thermocouple and potentiometer; operation of this equipment is rather straight forward although several points should be checked to ensure accurate measurement. The thermocouple connecting wires should be securely tightened to the terminal lugs on the potentiometer, and it should be determined that the thermocouple circuit is complete (an open circuit will be evident if the potentiometer fails to balance, giving readings off the scale of the instrument). If the potentiometer being used is not an automatic compensating type (automatic reference to ambient temperature), see that the ambient air temperature has been recorded or that the potentiometer scale has been calibrated with this temperature as a reference. While taking gas temperature readings, sufficient time should be allowed (normally about five minutes) for the thermocouple probe to reach thermal equilibrium with the duct gas before taking the first few readings.

As part of the data necessary for the velocity determination, the static pressure within the stack or duct should be measured. This is done using a mercury-filled "U" tube manometer, one end of which is open to the atmosphere and the other connected to a probe extending into the duct or stack itself. Again, the tubing from the probe to the manometer must be free of constrictions and tightly connected at both ends. A barometric pressure reading (of atmospheric pressure) in inches of mercury, should be obtained from a standard barometer located in the general vicinity of the test site; this can be a wall-mounted barometer in the plant offices, laboratory, or any convenient location which is at ambient temperature and free to vibration.

6.3.3. Hydrogen Sulfide (EPA Method No. 11, Reference 2 and 6)

Hydrogen sulfide (H_2S) is sampled from the centroid (or a point near the center) of the fuel gas line. Inspectors should check to see that the probe is in the required position and that a sampling valve is placed in the probe just after it emerges from the refinery fuel gas line. A word of caution is in order here as the fuel gas line is often operated at high pressure and a pressure reducing valve probably will be found where the sample is to be taken, care should be exercised in opening this valve. The sample line immediately after the valve must be 1/4 inch Teflon tubing with provisions for heating in order to eliminate condensation of moisture from the sample as it is extracted from the gas line. The Teflon tubing must connect to a series of five (5) midget impingers (30 ml capacity each) which are fitted with ball and socket joints. Several points are important to check in connection with the impinger series: all connections must be air-tight and the ball joint connections must be greased and secured with proper size retaining spring-clips; 15 ml of 3 percent hydrogen peroxide should be placed in the first impinger; absorber solution must be placed in the next three (3) impingers (15 ml of the solution in each) with the fifth remaining empty; an ice water bath must be in contact with the impingers in such a manner as to maintain the last (dry) impinger at 20°C (70°F). The absorbing solution has a tendency to settle out; be sure that this solution in the impingers is well in-suspension before sampling begins.

Immediately after the impinger series is a silica gel drying tube followed by a needle valve, pump (pump can be eliminated if refinery fuel gas line has sufficient pressure to drive gas through the sampling train), rotameter, and finally a dry gas meter. The sample line should be purged and the initial sampling rate should be set at 1.13 liters per minute.

No samples shall be taken in less than 10 minutes and some fuel gas lines in which the concentration of H_2S is low will require longer sampling periods. Bear in mind that the collection of H_2S is evident by formation of the yellow CdS precipitate. Minimum sample volume is 0.01 dry standard cubic meters (0.35 dscf) per sample. The arithmetic average of two determinations constitutes one run, each determination being made at approximately one-hour intervals.

The following data should be recorded by inspectors in order to check results later: sampling time, gas volume collector; rotameter setting; and meter setting for each sample.

Before sampling, the line between the probe and the first impinger should be purged. Observe sample recovery methods and cleaning procedures between samplings. Make sure that the acidified iodine solution is used to wash out impingers and connecting glassware and that the washings are transferred directly into the iodine-number flask. The flask itself must be kept tightly stoppered at all times except when adding washings and this must be completed as rapidly as possible to avoid loss of iodine vapor.

6.3.4 Sulfur Dioxide (EPA Method No. 6, Reference 6)

This method is applicable for the determination of sulfur dioxide emissions from stationary sources when specified by the test procedures for determining compliance with New Source Performance Standards. Method 1, as discussed in Section 6.3.1, is used for velocity traverses and Method 2 (Section 6.3.2) for determining velocity and volumetric flow rate. The sampling site for determining SO_2 concentration by Method 6 is the same as for determining volumetric flow rate by Method 2.

The sampling point in the duct for determining SO_2 concentration by this Method 6 is at the centroid of the cross section if the cross sectional area is less than 5 m^2 (54 ft^2) or at a point no closer to the walls than 1 m (39 inches) if the cross sectional area is 5 m^2 or more and the centroid is more than one meter from the wall. Inspectors should check to see that the probe is in the required position. Inspectors should also check to see if the Pyrex glass probe is equipped with heating system to prevent condensation and a filtering medium to remove particulate matter including sulfuric acid mist.

The sample line is connected to a midget bubbler and three midget impingers in series. The midget bubbler should be checked for the glass wool packing in the top part to prevent sulfuric acid mist carryover. Several points are important to check in connection with the impinger series: all connections must be air-tight and the ball joint connections must be secured with proper size retaining spring-clips; 15 ml of 80% isopropanol must be placed into the midget bubbler and 15 ml of 3% hydrogen peroxide into each of the first two midget impingers with the fourth one dry (remaining empty); an ice water bath must be in contact with the impingers in such a manner so as to keep the temperature of the gases leaving the last impinger at 21°C (70°F) or less.

Inspectors should make sure that a leak check test run of the sampling train at the sampling site is conducted by plugging the probe inlet and pulling a 10 inches Hg vacuum. After plugging or pinching off the outlet of the flowmeter, the pump should be turned off. The vacuum should remain constant for one minute.

Immediately after the impinger series is a silica gel drying tube followed by a pump, needle valve, rotameter, and finally a dry gas meter along with a thermometer. The sample is extracted at a rate proportional to the gas velocity at the sampling point. No samples shall be taken in less than 10 minutes and the minimum sampling volume shall be 0.01 dscm (0.35 dscf) for each sample. The arithmetic average of two samples shall constitute one run. Samples shall be taken at approximately 1-hour intervals.

The following data should be recorded by the inspectors in order to check the results later:

- Sample volume measured by the dry gas meter, cu m (cu ft)
- Average dry gas meter temperature, ^{o}K (^{o}R)
- Barometric pressure at the orifice meter, mm Hg (inch Hg)

The inspector should also observe the sample recovery methods and cleaning procedures between samplings. The contents of the midget bubbler is discarded while the contents of the midget impingers are poured into a polyethylene shipment bottle. The midget impingers and the connecting tubes are rinsed with the distilled water and these washings are added to the same storage container.

6.4 EMISSIONS MONITORING

6.4.1 H_2S Monitoring

No specific method for H_2S emission monitoring has been specified by EPA, however, continuous monitoring for H_2S in acid gas treatment plants can be accomplished by a monitor in the treated gas line (return of treated gas to refinery fuel gas supply). Since hydrogen sulfide monitoring is a new technique, the majority of Acid Gas Treatment Plants will not be equipped with continuous monitoring instrumentation for hydrogen sulfide.

On those installations which are so equipped, the technique of extractive sampling will be used. Of those systems which are in use, the electrochemical cell is most widely used, followed by flame photometric (specific for sulfur). Currently no practical in-situ methods are employed.

The sample extraction portions of all of these systems will be basically alike and, all should be equipped with filtering devices to eliminate particulate matter and moisture. The probe should be constructed of Teflon, Vycor, or stainless steel, but not of reactive materials such as copper, brass, or aluminum. Provision should be made for periodic purging and/or cleaning of the sampling probe. Any optical surfaces or mirrors must be kept clean and in good repair. A regular routine maintenance program must be carried out in order to keep the system operating at its designed level of reliability.

The analytical or detector portions of the various systems are slightly different from one another in that the electrochemical cell is a small, "black box" unit which is essentially self-contained,

while the flame photometric type is a larger unit which depends upon external fuel supplies in order to carry out its analysis. The electrochemical cell utilizes a semi-permeable membrane through which a portion of the H_2S passes into the cell. In the cell, electro-oxidation of the gas produces an electric signal at a rate directly proportional to the concentration of the gas in the sample.

The flame photometric system uses a photomultiplier tube and filter specific for detection of excited short-term sulfur emissions. The sample itself is burned to achieve the necessary excitation for the detector tube. This method responds positively to other sulfur-containing compounds. The detector should be checked for cleanliness of the optical surfaces as well as the adequacy of supply and quality of the fuel gas. The burner in this type of detector is especially prone to gathering dirt and ash, so extra care should be taken to see that these areas are regularly cleaned. Inspection of electro-chemical cell detectors should include checking the completeness of the cell (particularly the semi-permeable membrane and gasketing).

Data recording devices should be equipped with an alarm provision to sound when H_2S level reaches a predetermined level, in this case 230 mg/dNm^3 (0.10 gr/dscf). The detector portions of these monitoring systems should be located fairly close to the sampling site, but should be free of vibration, heat, shock, protected from the weather, and should provide safe convenient access for purposes of calibration and maintenance.

Calibration must be carried out at least once in every 24 hour period unless the manufacturer suggests a more frequent calibration interval, in which case his suggestions must be followed. If possible, inspectors should arrange for a demonstration of the alarm system by "doping" the sampling inlet with a heavy concentration of H_2S, for the purpose of determining that the feature is effective.

If a monitoring system is encountered which is not covered in this manual, inspectors should first ascertain the principle involved in its operation. With this information at hand, an effective inspection can then be made of the sampling and analysis

portions of the system. The data recording and alarm systems will be basically alike. A few points to check are listed as follows:

1) Probe material; make certain it is a non-reactive material and that adequate provision exists for cleaning and/or purging the probe.

2) Any optical surfaces should be in some manner protected from direct exposure to stack gases and, a filtering system to exclude moisture and particulate material should be included in the sample extraction portion.

3) The analytical portion of the system should be so located as to minimize its exposure to vibration, shock weather, and dirt. Safe, convenient access should be provided for purposes of calibration and maintenance.

4) Inspectors should determine frequency of calibration, cleaning, and routine maintenance.

5) Data recording system must be operational and an alarm feature should be incorporated to sound when pollutant being monitored reaches a predetermined level. A demonstration of this feature in operation should be observed.

6.4.2 SO_2 Monitoring

The direction of current developments indicates that common usage for SO_2 emission monitoring may settle on certain types of automatic physical-chemical and electro-optical instrumentation. There are three basic approaches to source monitoring that could foreseeably meet the current requirements of the EPA.

- Extract a continuous sample from the stack or duct and feed it to any appropriate analytical instrument, after initial conditioning by means of a sample handling/interface system.

- Observe and analyze the stack gas in situ by means of an optical instrument whose light path traverses the gases inside the stack or duct.

- Observe and analyze the stack gases shortly after they leave the stack, by means of a remote optical instrument.

In the extractive approach, a continuous sample is drawn from the stack and transported to the analyzer, which can be mounted in any convenient location. This requires a probe mounted in the stack or duct, and some form of interface system to provide the analyzer with a sample that is in an appropriate state of cleanliness, temperature, pressure, and moisture content. This approach is the oldest and has provided the most experience to date.

With the in situ approach, the instrument is mounted either inside, or just outside the stack. In the case of photometric and spectroscopic instruments, the light source may be mounted on one side of the stack and the detector on the other, or else the instrument may incorporate an extended mechanical beam with a mirror on the end or a mirror may be mounted on the opposite side of the stack so that the light penetrates a fixed distance and is returned to the instrument on the same side. Since these spectroscopic instruments determine pollutant concentrations by their discrete spectral absorption, they must be capable of discriminating against absorption and scattering of the light by particulates. They must also have high discrimination against all other, unwanted, components that are present in the stack gas, such as water vapor or carbon dioxide.

The in situ approach provides an average reading across the whole stack which may be considered an advantage over the point sampling approach that is most common with the extractive systems. It is possible, however, to provide the averaging function with the extractive system by using multiple integrating probes.

One problem facing all in situ optical instruments is that of keeping the optical windows clean. The common solution is to bathe the windows with a stream of clean air. This appears to be fairly effective for a reasonable period of time, but periodic mechanical cleaning is required. Another problem with the in situ instruments is to provide a satisfactory method of checking zero and span periodically. This is normally done with most analytical instruments by supplying known blends of zero and span gases to the instrument. This is not as practical with in situ monitors, as it is with extractive systems.

In order to check the SO_2 monitoring instrument, inspectors are recommended to collect information prior of the inspection regarding the type of SO_2 monitoring instrument used including a manual about the instrument-system and study the problems associated with the system used. As a general practice, to ensure that all of the apparatus is working properly, stack

gas results obtained from EPA Method 6 should be compared to those from monitoring data. Instruments and sampling systems installed and used shall meet specifications prescribed by the Administrator and each instrument shall be calibrated in accordance with the method prescribed by the manufacturer of the instrument. Inspectors should check to see if zero adjustment is done according to manufacturer's recommended procedure and that calibration procedures are performed at least once per 24-hour operating period or at short intervals as specified by the manufacturer.

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